

# Supplementary Conjugated Circuits for Biphenylene and related hydrocarbons

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### Abstract

Individual Kekulé valence structures of biphenylene and related hydrocarbons are comparatively studied in respect of their total pi-electron energies and thereby relative stabilities. These structures are modelled as sets of weakly-interacting initially-double (C=C) bonds. The relevant total energies are represented in the form of power series, wherein the averaged resonance parameter of initially-single (C–C) bonds underlies the expansion. To rationalize the resulting distinctions in total energies, interrelations are sought between separate members of the series, on the one hand, and presence of definite substructures in the given Kekulé valence structure, on the other hand. It is shown that monocycles  $S_1$  and  $S_2$  correspondingly containing two and four exocyclic methylene groups [like 3,4-dimethylene cyclobutene and [4]radialene] participate in the formation of energy corrections of the relevant Kekulé valence structures along with the usual conjugated circuits of the  $4n + 2$  and  $4n$  series ( $R_n$  and  $Q_n, n = 1, 2, 3, \dots$ ). Thus, the cycles  $S_1$  and  $S_2$  are deductively predicted to play the role of supplementary conjugated circuits for biphenylene-like hydrocarbons. Moreover, the  $S_2$ – and  $S_1$ – containing structures are shown to be the most stable ones among all Kekulé valence structures of the given hydrocarbon. Meanwhile, the lowest stability is predicted for structures in which either the neighboring hexagonal rings are connected by two C=C bonds or two exocyclic C=C bonds are attached to the same hexagonal ring.

### 1. Introduction

Stabilities of pi-electron systems of monocyclic hydrocarbons (annulenes) are known to be governed by the Hückel ( $4n + 2$ ) rule (see e.g. [1, 2]), which predicts an increased stability (and thereby aromaticity) of compounds having 6, 10, 14, .. carbon atoms and/or pi-electrons vs. those of the  $4n$  series, viz.  $C_4H_4$ ,  $C_8H_8$ , etc. For polycyclic molecules, however, such a simple and universal rule has been not yet formulated in spite of numerous attempts in this direction. Particular rules based on total numbers either of Kekulé valence structures of the given compound (cf. the Kekulé structure count [3-6]) or of the aromatic sextets (cf. the Clar aromatic sextet (CAS) model [7-9]) may be referred to here as the most well-known examples of early qualitative approaches to stabilities of polycyclic hydrocarbons. Later and more sophisticated treatments of the same problem, in turn, may be exemplified by the theory of cyclic conjugation [10] and by that of conjugated circuits [11-15]. Although stability of a certain polycyclic system is discussed in terms of contributions of individual monocycles in both theories, the underlying models differ one from another significantly: Pi-electron subsystems of (poly)cyclic hydrocarbons are assumed to contain uniform carbon-carbon bonds as usual in the theory of cyclic

conjugation (cf. the molecular graph [15, 16]), whereas conjugated circuits are defined as cycles consisting of strong (C=C) and weak (C–C) bonds alternately and thereby refer mainly to separate Kekulé valence structures of the given hydrocarbon [15]. Again, the above-mentioned definition allowed a fruitful analogy to be traced [17] between the theory of conjugated circuits [abbreviated below as the CC theory] and the perturbative treatment of pi-electron systems of conjugated hydrocarbons based on a model of weakly-interacting initially-double (C=C) bonds [18]. Moreover, this analogy along with the earlier-derived power series for total energies of molecules [19] resulted into an original perturbative approach [17, 20, 21] that exhibited an additional cognitive and discriminative potential vs. that of the CC theory. The present contribution contains a continuation of studies in this direction.

The CC theory of polycyclic conjugated hydrocarbons is currently under an intensive development [22-33] and its principal achievements are discussed in the review [15]. This theory was especially successful for benzenoid hydrocarbons having conjugated circuits of the  $4n+2$  series only as proven in [23] [these circuits are usually designated by  $R_n$  ( $n=1,2,\dots$ ), where  $R_1$  coincides with a single Kekulé valence structure of benzene,  $R_2$  embraces five C=C and five C–C bonds alternately, etc.]. So far as non-benzenoid hydrocarbons, in general, and biphenylene-like systems, in particular, are concerned, the results of the same theory proved to be considerably less satisfactory [15, 33]. This especially refers to the simplest version of the CC theory, wherein all Kekulé valence structures of the given compound are assumed to be of the same "weight". Otherwise, reliable criteria are required to discriminate between importances of separate structures. Unfortunately, different criteria sometimes yield contradictory conclusions [15, 34].

Biphenylene and its derivatives (e.g. [N]phenylenes) [35] evidently are of a more involved constitution as compared to benzenoids. Indeed, these non-benzenoid molecules contain four-atomic rings along with the six-atomic ones and thereby conjugated circuits (CCs) of both  $R_n$  ( $4n+2$ ) and  $Q_n$  ( $4n$ ) series, the latter notation standing for circuits embracing even numbers of C=C (and thereby of C–C) bonds. Thus, an interplay of opposite factors is expected to determine the actual stabilities of pi-electron systems in this case [10, 36] [Six- and four-atomic rings are assumed to contribute to stabilization and to destabilization, respectively, in accordance with the Hückel  $[4n+2]$  rule]. Consequently, even the extent and the nature of aromaticity of the parent biphenylene are still under discussion [15, 36-38], to say nothing about its derivatives. Dependence of the total pi-electron energy upon the Kekulé structure count of phenylenes also were found to differ essentially from that of benzenoids [39, 40]. In this context, the above-discussed difficulties of the CC theory cause little surprise. To be able to foresee the most efficient ways of improvement of the theory, however, a more specific (preferably a deductive) accounting is highly desirable for its lower success in the case of biphenylene-like hydrocarbons. To achieve this end, just the above-mentioned perturbative approach seems to be helpful.

The total energy of a pi-electron system ( $\mathcal{E}$ ) has been expressed in this approach [17, 19-21] as a sum of steadily diminishing increments ( $\mathcal{E}_{(k)}$ ) of various orders ( $k$ ) with respect to the averaged resonance parameter ( $\gamma$ ) representing the weak (C–C) bonds. Application of this approach to isolated CCs ( $R_1$  and  $R_2$ ) indicated significant positive corrections of odd orders ( $\mathcal{E}_{(3)}$  and  $\mathcal{E}_{(5)}$ , respectively) to arise in

the relevant power series that are responsible for the excessive stability of these monocycles [Note that a negative energy unit was used]. Moreover, parallelism has been established between separate terms of the series for total energies of individual Kekulé valence structures of benzenoid hydrocarbons and the circuits  $R_n$  ( $n = 1, 2, \dots$ ) present there. Hence, the perturbative approach of Refs.[17, 19-21] proved to be a certain deductive analogue of the CC theory that is likely to make possible an independent verification of its principal assumptions. In this context, an important question naturally arises whether the standard circuits  $R_n$  and  $Q_n$  ( $n = 1, 2, \dots$ ) are the only important fragments (substructures) determining relative stabilities of individual Kekulé valence structures of hydrocarbons concerned. This point also is under focus of the present study.

In summary, our aim consists in application of the approach of Refs. [17, 19-21] to individual Kekulé valence structures of biphenylene-like hydrocarbons, as well as in a deductive revealing the principal fragments (substructures) determining their total energies and thereby relative stabilities.

The scheme of the paper is as follows: We start with an overview of the principal formulae of the perturbative approach (Sect. 2). Thereupon, we apply these formulae to individual Kekulé valence structures of biphenylene and of some related hydrocarbons (Sect. 3). The expected decisive substructures are considered separately in Section 4. Section 5 addresses the simplest combinations of these substructures, whilst the final Section (6) contains the conclusions.

## 2. The principal formulae of the perturbative approach

As already mentioned, the approach of Refs.[17, 19-21] addressed pi-electron systems of conjugated hydrocarbons containing two types of uniform bonds, namely strong (C=C) and weak (C–C) ones. The power series for total energies of these systems has been derived and analyzed previously. Thus, we will confine ourselves here to a brief overview of the principal definitions and formulae.

Let us start with the basis set  $\{\varphi\}$  underlying the series concerned and consisting of bond orbitals (BOs) of strong (C=C) bonds. The bonding BO (BBO) and the antibonding BO (ABO) of a certain C=C bond are correspondingly defined as a normalized sum and difference of pairs of  $2p_z$  AOs of carbon atoms involved in the given bond. These BOs will be denoted by  $\varphi_{(+)i}$  and  $\varphi_{(-)i}$ , respectively, where the subscript  $i$  refers to the  $i$ th C=C bond. Let the number of C=C bonds to coincide with  $N$ . The set of BOs  $\{\varphi\}$  then accordingly contains  $2N$  basis functions.

The power series for total energies of the above-specified pi-electron systems ( $\mathcal{E}$ ) takes the form

$$\mathcal{E} = \sum_{k=0}^{\infty} \mathcal{E}_{(k)} \quad (1)$$

and contains the following starting members

$$\mathcal{E}_{(0)} = 2N, \quad \mathcal{E}_{(1)} = 0, \quad \mathcal{E}_{(2)} = 4Tr(\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+), \quad \mathcal{E}_{(3)} = 4Tr(\mathbf{G}_{(2)}\mathbf{G}_{(1)}^+), \quad (2)$$

where  $Tr$  stands here and below for the *Trace* of the whole matrix product within parentheses, the superscript  $+$  designates a transposed (Hermitian-conjugate) matrix, and  $\mathbf{G}_{(1)}$  and  $\mathbf{G}_{(2)}$  are the principal matrices of our expansion of the first and

second orders, respectively [The order is defined with respect to parameter  $\gamma$  as demonstrated below]. Let  $\mathbf{S}$ ,  $\mathbf{Q}$  and  $\mathbf{R}$  stand for matrices, individual elements of which represent distinct types of interactions (resonance parameters) between BOs, viz.

$$\begin{aligned} \mathbf{S}_{ij} &= \langle \varphi_{(+i)} | \hat{H} | \varphi_{(+j)} \rangle, & \mathbf{R}_{il} &= \langle \varphi_{(+i)} | \hat{H} | \varphi_{(-l)} \rangle, \\ \mathbf{Q}_{lm} &= \langle \varphi_{(-l)} | \hat{H} | \varphi_{(-m)} \rangle, \end{aligned} \quad (3)$$

where the orbitals concerned are shown inside the bra- and ket-vectors. The principal matrices  $\mathbf{G}_{(1)}$  and  $\mathbf{G}_{(2)}$  are then expressible via matrices  $\mathbf{S}$ ,  $\mathbf{Q}$  and  $\mathbf{R}$ , viz.

$$\mathbf{G}_{(1)} = -\frac{1}{2}\mathbf{R}, \quad \mathbf{G}_{(2)} = \frac{1}{4}(\mathbf{SR} - \mathbf{RQ}) = \frac{1}{4}(\mathbf{SR} + \mathbf{RS}), \quad (4)$$

where the last relation is based on the equality  $\mathbf{S} = -\mathbf{Q}$  valid for even alternant hydrocarbons [1, 2] [Kekulé valence structures to be studied belong to].

In contrast to the simple and unique formulae for  $\mathcal{E}_{(2)}$  and  $\mathcal{E}_{(3)}$  shown in Eq.(2), alternative expressions are possible for the relevant fourth order term  $\mathcal{E}_{(4)}$ . Let us dwell here on the formula for  $\mathcal{E}_{(4)}$  in the form of a sum of two components of opposite signs [20], viz. of the positive component ( $\mathcal{E}_{(4)}^{(+)}$ ) and of the negative one ( $\mathcal{E}_{(4)}^{(-)}$ ) defined as follows

$$\mathcal{E}_{(4)}^{(+)} = 4Tr(\mathbf{G}_{(2)}\mathbf{G}_{(2)}^+) > 0, \quad \mathcal{E}_{(4)}^{(-)} = -4Tr(\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+) < 0. \quad (5)$$

To make the application of Eqs.(1)-(5) to pi-electron systems of Kekulé valence structures more convenient, direct expressions are desirable for matrices  $\mathbf{S}$ ,  $\mathbf{Q}$  and  $\mathbf{R}$  (and thereby for  $\mathbf{G}_{(1)}$  and  $\mathbf{G}_{(2)}$ ) in terms of submatrices (blocks) of the relevant initial Hamiltonian matrix represented in the basis of  $2p_z$  AOs of carbon atoms  $\{\chi\}$  as usual. Let us dwell now just on these expressions.

Let the  $2p_z$  AOs be characterized by uniform Coulomb parameters ( $\alpha$ ). Moreover, uniform resonance parameters ( $\beta$ ) are supposed to correspond to any C=C bond in the basis  $\{\chi\}$ . Let us also accept the usual equalities  $\alpha = 0$  and  $\beta = 1$ , the latter implying a negative energy unit to be actually chosen. The total  $2N$ -dimensional basis set  $\{\chi\}$  of an even alternant hydrocarbon is known to be divisible into two  $N$ -dimensional subsets  $\{\chi^*\}$  and  $\{\chi^\circ\}$  so that pairs of AOs belonging to any chemical bond (either C=C or C-C) find themselves in different subsets [1, 2, 41-43]. This implies non-zero resonance parameters representing chemical bonds to take place in the off-diagonal (intersubset) positions of the initial Hamiltonian matrix ( $\mathbf{H}$ ) [41-43]. Let these blocks to be denoted by  $\mathbf{H}_{*o}$ . Given that pairs of AOs belonging to the same (say  $i$ th) C=C bond acquire coupled numbers  $i$  and  $N + i$  in addition, resonance parameters of these strong bonds (coinciding with our energy unit  $\beta$ ) take the diagonal positions of the blocks  $\mathbf{H}_{*o}$  and thereby compose a unit matrix ( $\mathbf{I}$ ). We then obtain that

$$\mathbf{H}_{*o} = \mathbf{I} + \gamma\mathbf{B}, \quad (6)$$

where the matrix  $\mathbf{B}$  contains unit elements in the positions referring to C-C bonds and zero elements elsewhere. Meanwhile,  $\gamma$  represents the averaged resonance parameter of C-C bonds that is supposed to take a small value in our energy units. The above-introduced matrices  $\mathbf{S}$ ,  $\mathbf{Q}$  and  $\mathbf{R}$  are then proportional to the symmetric

(Hermitian) and skew-symmetric (skew-Hermitian) parts of the matrix  $\mathbf{B}$ , respectively, viz.

$$\mathbf{S} = -\mathbf{Q} = \frac{\gamma}{2}(\mathbf{B} + \mathbf{B}^+), \quad \mathbf{R} = \frac{\gamma}{2}(\mathbf{B}^+ - \mathbf{B}). \quad (7)$$

The matrix  $\mathbf{B}$  is easily constructable for any Kekulé valence structure. Expressions of Eq.(7) then yield matrices of interbond resonance parameters ( $\mathbf{S}$ ,  $\mathbf{Q}$  and  $\mathbf{R}$ ), whilst Eq.(4) provides us with the relevant principal matrices  $\mathbf{G}_{(1)}$  and  $\mathbf{G}_{(2)}$  to be subsequently substituted into Eqs. (1), (2) and (5) to derive the total energy. The first and second orders of matrices  $\mathbf{G}_{(1)}$  and  $\mathbf{G}_{(2)}$  with respect to parameter  $\gamma$  easily follow from Eqs. (4) and (7). Moreover, the skew-symmetric (skew-Hermitian) nature of these matrices may be proven [43] that ensures vanishing diagonal elements  $\mathbf{G}_{(1)ii}$  and  $\mathbf{G}_{(2)ii}$  for any  $i$ .

Let us turn now to interpretation of the above formulae and start with elements of matrices  $\mathbf{G}_{(1)}$  and  $\mathbf{G}_{(2)}$  defined by Eq.(4). The first order element ( $\mathbf{G}_{(1)il}$ ) is proportional to the relevant resonance parameter ( $\mathbf{R}_{il}$ ) and represents the direct (through-space) interaction between the BBO  $\varphi_{(+)i}$  and the ABO  $\varphi_{(-)l}$ . Let pairs of C=C bonds connected by a C—C bond be regarded as first-neighboring. It is then evident that non-zero elements ( $\mathbf{G}_{(1)il} \neq 0$  and  $\mathbf{G}_{(1)li} \neq 0$ ) generally correspond to first-neighboring pairs of C=C bonds and/or to individual C—C bonds [This does not imply, however, that any C—C bond necessarily is represented by non-zero elements  $\mathbf{G}_{(1)il}$  and  $\mathbf{G}_{(1)li}$  as the results of Sect. 3 show]. Further, the second order elements  $\mathbf{G}_{(2)il}$  are accordingly interpretable as indirect (through-bond) interactions of the same BOs. Indeed, from Eq.(4) we obtain

$$\mathbf{G}_{(2)il} = \frac{1}{4} \left[ \sum_{(+)j} \mathbf{S}_{ij} \mathbf{R}_{jl} - \sum_{(-)m} \mathbf{R}_{im} \mathbf{Q}_{ml} \right], \quad (8)$$

where sums over  $(+)j$  and over  $(-)m$  correspondingly embrace BBOs ( $\varphi_{(+)j}$ ) and ABOs ( $\varphi_{(-)m}$ ). It is seen that BOs of other bonds play the role of mediators in the second order interaction between orbitals  $\varphi_{(+)i}$  and  $\varphi_{(-)l}$  [Note that elements  $\mathbf{S}_{ii}$ ,  $\mathbf{Q}_{ll}$  and  $\mathbf{R}_{ii}$  vanish]. Moreover, the orbitals  $\varphi_{(+)j}$  and  $\varphi_{(-)m}$  should overlap directly both with  $\varphi_{(+)i}$  and with  $\varphi_{(-)l}$  to be efficient mediators. That is why non-zero indirect interactions correspond to pairs of second-neighboring C=C bonds possessing a common first neighbor.

Let us dwell now on members of the power series for total energies. As is seen from the first relation of Eq.(2), the zero order member  $\varepsilon_{(0)}$  coincides with the total energy of  $N$  isolated C=C bonds in accordance with the expectation. The subsequent (second order) term  $\varepsilon_{(2)}$ , in turn, depends on the total number of non-zero direct interactions ( $\mathbf{G}_{(1)il}$ ) between BBOs and ABOs. In the usual case of two-to-one correspondence between significant elements  $\mathbf{G}_{(1)il}$  ( $\mathbf{G}_{(1)li}$ ) and C—C bonds [17, 21], the second order energy  $\varepsilon_{(2)}$  complies with the relation  $\varepsilon_{(2)} = N'\gamma^2/2$  [e.g.  $\varepsilon_{(2)}(R_1) = 3\gamma^2/2$  [17]], where  $\gamma^2/2$  is the contribution of a single C—C bond and  $N'$  here and below stands for the number of these bonds [Note that numbers  $N'$  and  $N$  generally do not coincide one with another]. The *a priori* positive sign of the second order energy  $\varepsilon_{(2)}$  and thereby its stabilizing nature also deserves adding here.

The third order member of the same series ( $\varepsilon_{(3)}$ ) is determined by products  $\mathbf{G}_{(2)il}\mathbf{G}_{(1)il}$  as Eq.(2) shows. This implies this member to take a non-zero value

if in the given system there is at least a single pair of BOs ( $\varphi_{(+)i}$  and  $\varphi_{(-)l}$ ) that interact both directly and indirectly by means of a single mediator. Since the latter necessarily belongs to a third (say, the Mth) C=C bond (that coincides neither with the Ith bond nor with the Lth one), we arrive at a condition of presence of at least a single triplet of C=C bonds, the BOs of all pairs of which interact (overlap) directly, i.e. of a triplet I, L, M, wherein all three pairs of C=C bonds are first-neighboring. In the case of Kekulé valence structures of benzenoids, any circuit  $R_1$  evidently offers a required triplet. Consequently, the relevant third order energies proved to be additive quantities with respect to transferable increments of individual CCs  $R_1$ , each of these increments coinciding with  $\varepsilon_{(3)}(R_1) = 3\gamma^3/4$  [17]. Given that  $K$  stands for the total number of the circuits  $R_1$  in the given Kekulé valence structure, the correction concerned meets the relation  $\varepsilon_{(3)} = 3\gamma^3 K/4$ . Conditions determining the sign of the third order energy also easily follow from the last formula of Eq.(2). Indeed, a particular product  $\mathbf{G}_{(2)il} \mathbf{G}_{(1)il}$  yields a positive (negative) contribution to the total correction  $\varepsilon_{(3)}$ , if the participating interbond interactions (i.e. both  $\mathbf{G}_{(2)il}$  and  $\mathbf{G}_{(1)il}$ ) are of the same (opposite) sign(s). In particular, positive products  $\mathbf{G}_{(2)il} \mathbf{G}_{(1)il}$  only were shown to refer to any circuit  $R_1$  in the Kekulé valence structures of benzenoid hydrocarbons [17].

Finally, the fourth order correction  $\varepsilon_{(4)}$  remains to be discussed. As is seen from Eq.(5), the positive component  $\varepsilon_{(4)}^{(+)}$  (that is stabilizing in our energy units) is determined by squares of indirect interbond interactions  $\mathbf{G}_{(2)il}$ . Meanwhile, the relevant destabilizing component  $\varepsilon_{(4)}^{(-)}$  is proportional to the sum of squares of elements of the matrix  $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+$ . The latter elements are interpretable as indirect interactions between BBOs ( $\varphi_{(+)i}$  and  $\varphi_{(+)j}$ ) via ABOs playing the role of mediators. In this connection, elements  $\mathbf{G}_{(2)il}$  and  $(\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+)_{ij}$  may be correspondingly referred to as stabilizing and destabilizing indirect interactions. Accordingly, both the absolute value and the sign of the correction  $\varepsilon_{(4)}$  is determined by the balance between the above-specified two types of interactions. It is no surprise in this connection that the overall relations between the fourth order energies  $\varepsilon_{(4)}$  and the presence of individual CCs proved to be much more involved as compared to the above-discussed direct relation between  $\varepsilon_{(3)}$  and the number of the circuits  $R_1$  ( $K$ ). For isolated circuits  $R_n$  ( $n=1,2,..$ ), however, two simple rules have been established [17]: First, all these circuits are characterized by positive corrections  $\varepsilon_{(4)}$ , i.e.  $\varepsilon_{(4)}(R_n) > 0$  for any  $n$ . Second, the corrections concerned are equal to  $2\gamma^4 N/64$ , where  $2\gamma^4/64$  is the contribution of a single C=C (or C–C) bond. This relation may be exemplified by the fourth order energy of an isolated circuit  $R_1$ , viz.  $\varepsilon_{(4)}(R_1) = 6\gamma^4/64$  [Note that  $\gamma^4/64$  has been chosen as a convenient "subsidiary" unit for fourth order energies [17]].

### 3. Total energies of Kekulé valence structures of biphenylene and related hydrocarbons

Let us start with biphenylene itself (I). The four symmetry-non-equivalent Kekulé valence structures of this hydrocarbon (I/I, I/II, I/III and I/IV) are shown in Fig.1 along with their compositions in terms of standard CCs  $R_n$  and  $Q_n$  ( $n = 1, 2, ...$ ). Since these CCs correspondingly embrace odd and even numbers of C=C bonds, these are conveniently referred to below as odd- and even-membered CCs. Moreover,

all Kekulé valence structures of Fig. 1 contain six C=C bonds ( $N = 6$ ) and eight C—C bonds ( $N' = 8$ ). [It deserves attention that  $N \neq N'$ ].

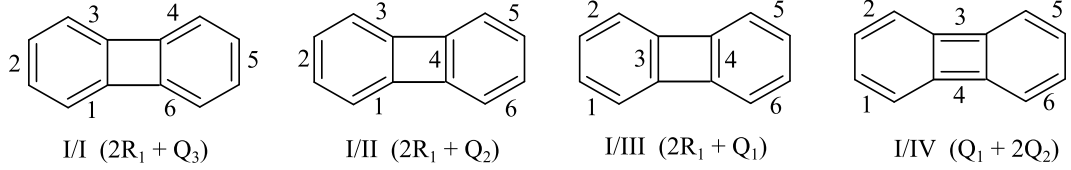


Figure 1: Symmetry-non-equivalent Kekulé valence structures of biphenylene (I) along with their compositions in terms of standard conjugated circuits  $R_n$  and  $Q_n$ ,  $n = 1, 2, \dots$ . Numbers of C=C bonds also are shown.

Zero order energies of structures I/I-I/IV coincide with 12 in our negative energy units (see Eq.(2)). The subsequent non-zero energy corrections are as follows

$$\varepsilon_{(2)}(I/I) = \varepsilon_{(2)}(I/II) = 4\gamma^2, \quad \varepsilon_{(2)}(I/III) = \varepsilon_{(2)}(I/IV) = 3\gamma^2, \quad (9)$$

$$\varepsilon_{(3)}(I/I) = \varepsilon_{(3)}(I/III) = \frac{6\gamma^3}{4}, \quad \varepsilon_{(3)}(I/II) = \frac{5\gamma^3}{4}, \quad \varepsilon_{(3)}(I/IV) = 0, \quad (10)$$

$$\varepsilon_{(4)}(I/I) = 0, \varepsilon_{(4)}(I/II) = -\frac{28\gamma^4}{64}, \varepsilon_{(4)}(I/III) = \frac{44\gamma^4}{64}, \varepsilon_{(4)}(I/IV) = -\frac{20\gamma^4}{64} \quad (11)$$

It is seen that second order energies of separate Kekulé valence structures of biphenylene are not uniform in spite of the same number of C—C bonds ( $N'$ ). Moreover, the usual relation  $\varepsilon_{(2)} = N'\gamma^2/2$  (Sect. 2) is met by the first two corrections (viz.  $\varepsilon_{(2)}(I/I)$  and  $\varepsilon_{(2)}(I/II)$ ) but not by the remaining ones ( $\varepsilon_{(2)}(I/III)$  and  $\varepsilon_{(2)}(I/IV)$ ) that are lower by  $\gamma^2$  vs. the former. This implies a certain exceptional second order destabilization to take place in the last two Kekulé valence structures of biphenylene. Since the latter contain a circuit  $Q_1$  in contrast to structures I/I and I/II, the destabilization concerned may be assumed to be related to the presence of just these simplest even-membered CCs.

Let us comment now the remaining relations of Eq.(10). The corrections  $\varepsilon_{(3)}(I/I)$ ,  $\varepsilon_{(3)}(I/III)$  and  $\varepsilon_{(3)}(I/IV)$  now comply with the usual relation between the third order energy ( $\varepsilon_{(3)}$ ) and the total number  $K$  of the simplest odd-membered circuits  $R_1$  (Sect. 2), where  $K$  coincides with 2, 2 and 0, respectively. Meanwhile, the second structure of biphenylene (I/II) is an exception in this respect. Indeed, the correction  $\varepsilon_{(3)}(I/II)$  is lower vs. that following from the relation  $\varepsilon_{(3)} = 3\gamma^3 K/4$  for  $K = 2$ . This fact gives us a hint that some additional structural factor(s) and/or substructure(s) exert a destabilizing influence upon the third order energy  $\varepsilon_{(3)}(I/II)$ . An important point here is that the even-membered conjugated circuit  $Q_2$  of the structure I/II hardly is able to play the above-anticipated role, as it does not offer a necessary triplet of first-neighboring C=C bonds (Sect. 2). Finally, the lowest (negative) fourth order energies are peculiar to the  $Q_2$ -containing structures I/II and I/IV. Thus, a certain fourth order destabilization may be assumed to take place due to the presence of a four-membered circuit  $Q_2$ . Meanwhile, the highest (positive) correction  $\varepsilon_{(4)}(I/III)$  refers to the structure I/III containing the simplest CCs  $R_1$  and  $Q_1$  only.

In summary, the above results suggest the following order of relative stability for the Kekulé valence structures of biphenylene:  $I/I > I/II > I/III > I/IV$  [Note that sums of second and third order energies actually are sufficient to discriminate between the structures concerned]. Applications of other criteria also yield the same conclusion, e.g. comparison of contributions of separate Kekulé valence structures to the resonance energy of biphenylene [15], as well as invoking of additional concepts, such as parity [44], innate degrees of freedom [45] and Kekulé index [46, 47] of a Kekulé valence structure. Finally, a similar order of stability has been established recently on the basis of a modified Hess-Schaad group additivity scheme [36].

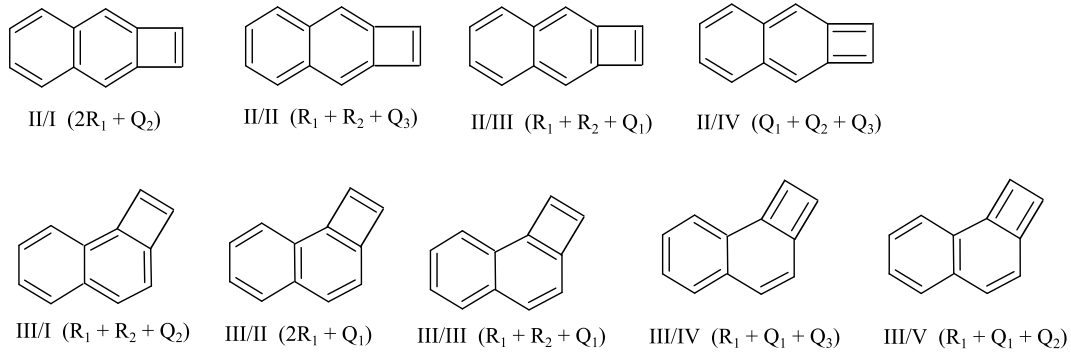


Figure 2: Kekulé valence structures of naphthocyclobutenes (II) and (III) along with their compositions in terms of standard conjugated circuits  $R_n$  and  $Q_n$ ,  $n = 1, 2, \dots$

Let us turn now to the naphthocyclobutene (II) and consider its Kekulé valence structures II/I-II/IV (Fig. 2). Zero order energies of these structures also are equal to 12 so that their stabilities are directly comparable to those of the former structures of biphenylene. Further, the  $Q_1$ -containing structures II/III and II/IV are characterized by an exceptionally low second order energy in this case as well, viz.

$$\varepsilon_{(2)}(II/I) = \varepsilon_{(2)}(II/II) = 4\gamma^2, \quad \varepsilon_{(2)}(II/III) = \varepsilon_{(2)}(II/IV) = 3\gamma^2 \quad (12)$$

and the destabilization effect coincides with  $\gamma^2$  as previously. For the relevant third order corrections, we obtain

$$\varepsilon_{(3)}(II/I) = \frac{5\gamma^3}{4}, \quad \varepsilon_{(3)}(II/II) = \frac{2\gamma^3}{4}, \quad \varepsilon_{(3)}(II/III) = \frac{3\gamma^3}{4}, \quad \varepsilon_{(3)}(II/IV) = 0. \quad (13)$$

It is seen that third order energies  $\varepsilon_{(3)}(II/I)$  and  $\varepsilon_{(3)}(II/II)$  are now exceptionally lowered vs. the anticipated values for  $K = 2$  and  $K = 1$ , respectively. Nevertheless, the correction  $\varepsilon_{(3)}(II/I)$  of the  $2R_1$ -containing structure II/I exceeds that of the  $R_1$ -containing one ( $\varepsilon_{(3)}(II/II)$ ) and, consequently, the resulting order of stability is expected to be as follows:  $II/I > II/II > II/III > II/IV$ . This order coincides with that following from Kekulé indices [46]. Finally, the relevant fourth order



energies take the form

$$\begin{aligned}\varepsilon_{(4)}(II/I) &= -\frac{28\gamma^4}{64}, & \varepsilon_{(4)}(II/II) &= \frac{16\gamma^4}{64}, & \varepsilon_{(4)}(II/III) &= \frac{32\gamma^4}{64}, \\ \varepsilon_{(4)}(II/IV) &= -\frac{4\gamma^4}{64},\end{aligned}\tag{14}$$

wherein the lowest (negative) values refer to  $Q_2$ -containing structures (II/I and II/IV) in this case too. Meanwhile, the fourth order energy of the structure II/III takes the highest (positive) value. In this respect, similarity between Kekulé valence structures I/III and II/III is evident. Since the latter contain the simplest circuits  $R_1$  and  $Q_1$ , the neighboring pairs of which possess a single common  $C=C$  bond, the high (positive) values of the fourth order energies  $\varepsilon_{(4)}(I/III)$  and  $\varepsilon_{(4)}(II/III)$  may be expected to originate just from this common aspect of constitution. Furthermore, the structures I/II and II/I offer us an example of uniform corrections referring to distinct hydrocarbons, namely these structures prove to be isoenergetic to within fourth order terms inclusive. Besides, the relevant compositions in terms of standard CCs ( $2R_1+Q_2$ ) also are uniform.

Our next example coincides with the bent isomer of naphthocyclobutene (III) characterized by five Kekulé valence structures III/I-III/V (Fig. 2), where  $N = 6$  and  $N' = 8$ . The number of  $Q_1$ -containing structures also is higher here, and this fact is reflected in the relevant second order energies, viz.

$$\varepsilon_{(2)}(III/I) = 4\gamma^2, \varepsilon_{(2)}(III/II) = \varepsilon_{(2)}(III/III) = \varepsilon_{(2)}(III/IV) = \varepsilon_{(2)}(III/V) = 3\gamma^2.\tag{15}$$

It is seen that the only  $Q_1$ -free structure (III/I) is described by a "normal" energy correction in this case. The relevant third order energies are as follows

$$\begin{aligned}\varepsilon_{(3)}(III/I) &= \frac{2\gamma^3}{4}, & \varepsilon_{(3)}(III/II) &= \frac{6\gamma^3}{4}, \\ \varepsilon_{(3)}(III/III) &= \varepsilon_{(3)}(III/IV) = \varepsilon_{(3)}(III/V) = \frac{3\gamma^3}{4}\end{aligned}\tag{16}$$

and the correction  $\varepsilon_{(3)}(III/I)$  now takes a lowered value as compared to that following from the relation  $\varepsilon_{(3)} = 3\gamma^3 K/4$  for  $K = 1$ . Moreover, sums of energy increments of second and third orders are insufficient to discriminate between all Kekulé valence structures of the bent isomer III, in contrast to the former hydrocarbons I and II. Fortunately, the relevant fourth order corrections take distinct values, viz.

$$\begin{aligned}\varepsilon_{(4)}(III/I) &= -\frac{20\gamma^4}{64}, & \varepsilon_{(4)}(III/II) &= \frac{28\gamma^4}{64}, & \varepsilon_{(4)}(III/III) &= \frac{32\gamma^4}{64}, \\ \varepsilon_{(4)}(III/IV) &= \frac{20\gamma^4}{64}, & \varepsilon_{(4)}(III/V) &= -\frac{8\gamma^4}{64}\end{aligned}\tag{17}$$

and thereby allow us to discriminate them. The result of Eq.(17) is even more surprising if we recall that the extended CCs neither  $R_2$  nor  $Q_3$  may be entirely embraced by corrections of the fourth order (the highest number of the embraced  $C=C$  bonds coincides with the order  $k$  of the relevant correction  $\varepsilon_{(k)}$ ). Equation (17) shows in addition that the lowest (negative) values of the fourth order energy refer

to  $Q_2$ -containing structures III/I and III/V as previously. Meanwhile, the remaining ( $R_1$  and  $Q_1$  -containing) structures III/II, III/III and III/IV are characterized by positive fourth order energies. The overall order of relative stabilities is then as follows:  $III/I > III/II > III/III > III/IV > III/V$ . An analogous conclusion has been drawn also on the basis of Kekulé indices [46] and connectivities of the relevant submolecules [48].

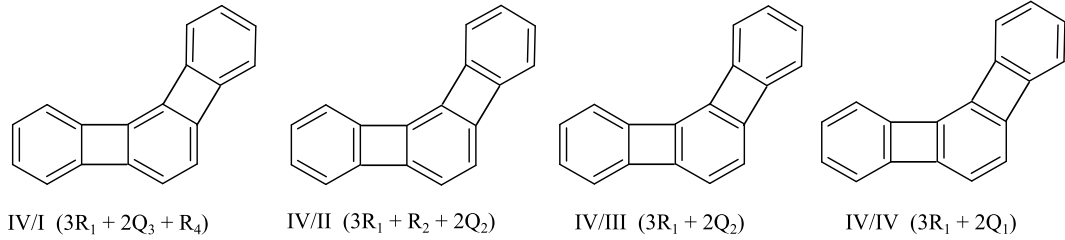


Figure 3: Selected Kekulé valence structures of bent [3]-phenylene along with their compositions in terms of standard conjugated circuits  $R_n$  and  $Q_n$ ,  $n = 1, 2, \dots$

Let us consider finally four selected Kekulé valence structures of bent [3]phenylene IV/I-IV/IV (Fig. 3), where  $N = 9$  and  $N' = 13$ . The common zero order energy of these structures accordingly equals to 18, whilst the second order corrections are as follows

$$\varepsilon_{(2)}(IV/I) = \varepsilon_{(2)}(IV/II) = \varepsilon_{(2)}(IV/III) = \frac{13}{2}\gamma^2, \quad \varepsilon_{(2)}(IV/IV) = \frac{9}{2}\gamma^2. \quad (18)$$

It is seen that the only  $Q_1$ -containing structure IV/IV is now characterized by an exceptionally lowered third order energy in accordance with the above-established trends. It is also noteworthy that the difference between corrections shown in Eq.(18) coincides with  $2\gamma^2$  instead of the former distinction  $\gamma^2$ . This fact is in line with two conjugated circuits  $Q_1$  contained in the structure IV/IV and thereby it supports the above assumption about the relation of the difference concerned to a destabilizing increment of just this circuit. The relevant third order energies, in turn, equal to

$$\varepsilon_{(3)}(IV/I) = \varepsilon_{(3)}(IV/IV) = \frac{9\gamma^3}{4}, \quad \varepsilon_{(3)}(IV/II) = \varepsilon_{(3)}(IV/III) = \frac{7\gamma^3}{4} \quad (19)$$

and take non-uniform values in spite of the same number of the circuits  $R_1$  ( $K = 3$ ) in the structures concerned. Moreover, two structures (viz. IV/II and II/III) are now characterized by lowered third order energies ( $7\gamma^3/4$ ) that do not follow from the standard relation for  $K = 3$  and, consequently, just the above-mentioned two exceptional structures cannot be discriminated before taking into account the relevant fourth order corrections. These are as follows

$$\begin{aligned} \varepsilon_{(4)}(IV/I) &= -\frac{2\gamma^4}{64}, & \varepsilon_{(4)}(IV/II) &= -\frac{58\gamma^4}{64}, & \varepsilon_{(4)}(IV/III) &= -\frac{62\gamma^4}{64}, \\ \varepsilon_{(4)}(IV/IV) &= \frac{82\gamma^4}{64} \end{aligned} \quad (20)$$

and indicate the structure IV/II to be a little bit less destabilized (and thereby more stable) as compared to IV/III. This result is in line with the presence of an additional "stabilizing" circuit  $R_2$  in the structure IV/II.

The overall set of fourth order energies of Eq.(20) also deserves some attention. Thus, the lowest (negative) values of these corrections (about  $-60\gamma^4/64$ ) refer to  $Q_2$ -containing structures (IV/II and IV/III) as previously, whereas the highest (positive) value ( $82\gamma^4/64$ ) corresponds to the  $(3R_1+2Q_1)$ -containing structure IV/IV. Meanwhile, the fourth order energy of the remaining structure (IV/I) takes an intermediate value. The latter, however, seems to be sufficiently low if we recall that the structure IV/I contains no "destabilizing" circuits  $Q_2$ . A more detailed discussion of this point is undertaken in Section 5. Summarizing the results of Eqs.(18)-(20) we may then conclude the predicted relative order of stabilities of the Kekulé valence structures under discussion to be as follows:  $IV/I > IV/II > IV/III > IV/IV$ . This expectation is in line with the actual contributions of the structures concerned to the molecular resonance energy [15, 34].

On the whole, two principal assumptions (hypotheses) follow from the results of this section: First, the even-membered conjugated circuits  $Q_1$  and  $Q_2$  seem to contribute to the second and fourth order destabilization, respectively, of the Kekulé valence structures concerned. Second, some additional factors (substructures) are likely to participate in the formation of third order energies of a part of Kekulé valence structures of biphenylene-like hydrocarbons (along with standard conjugated circuits  $R_1$ ) and thereby to be responsible for an extra third order destabilization of these structures. Our next aim consists in verification of these hypothesis and in revealing the above-anticipated additional substructures.

#### 4. Consideration of reference structures

The present section is devoted to isolated substructures that are expected to participate in the formation of the above-overviewed energy corrections. The odd-membered CCs ( $R_n$ ) have been studied previously in a detail [17] and the relevant energy increments are overviewed in Section 2. Thus, let us turn immediately to the even-membered CCs ( $Q_n$ , where  $n = 1, 2, \dots$ ).

##### 4.1. Even-membered conjugated circuits $Q_n$

Let us start with the simplest two-membered circuit  $Q_1$  (Fig. 4), where  $N = N' = 2$  and  $\mathcal{E}_{(0)}(Q_1) = 4$  (see Eq.(2)). The relevant matrix  $\mathbf{B}(Q_1)$  is as follows

$$\mathbf{B}(Q_1) = \gamma \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix}, \quad (21)$$

where unit elements represent resonance parameters of C–C bonds (viz.  $C_1-C_4$  and  $C_2-C_3$ ). The skew-symmetric part of this symmetric matrix evidently vanishes. From Eqs. (4) and (7), we then obtain

$$\mathbf{R}(Q_1) = \mathbf{G}_{(1)}(Q_1) = \mathbf{G}_{(2)}(Q_1) = \mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(Q_1) = \mathbf{0} \quad (22)$$

and

$$\mathcal{E}_{(2)}(Q_1) = \mathcal{E}_{(3)}(Q_1) = \mathcal{E}_{(4)}(Q_1) = 0. \quad (23)$$

If we recall here that the linear butadiene is characterized by a positive second order energy equal to  $\gamma^2/2$  [17, 20], destabilization in the circuit  $Q_1$  vs. its acyclic

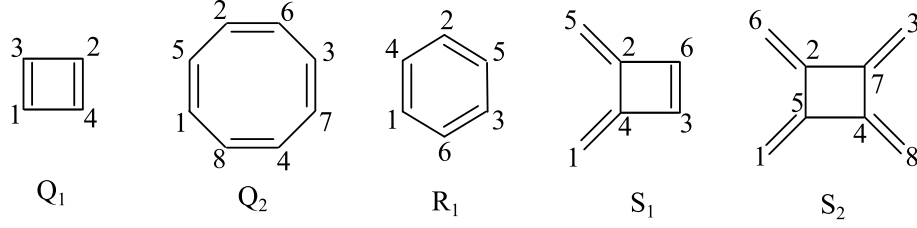


Figure 4: The simplest conjugated circuits of different series ( $R_n$ ,  $Q_n$  and  $S_n$ ). Numbers of carbon atoms and/or of their  $2p_z$  AOs also are shown.

analogue may be concluded. This result may be traced back to vanishing direct interactions between BBOs and ABOs of the circuit  $Q_1$  in contrast to the linear butadiene. Again, the zero second order energy  $\mathcal{E}_{(2)}(Q_1)$  seen from Eq.(23) seems to be inconsistent with the rule about each C–C bond contributing  $\gamma^2/2$  to the relevant total  $\mathcal{E}_{(2)}$  value (Section 2). To clarify this point, let us represent the matrix  $\mathbf{B}(Q_1)$  of Eq.(21) as a sum of two components

$$\mathbf{B}(Q_1) = \mathbf{B}^{(1-4)}(Q_1) + \mathbf{B}^{(2-3)}(Q_1) = \gamma \begin{vmatrix} 0 & 1 \\ 0 & 0 \end{vmatrix} + \gamma \begin{vmatrix} 0 & 0 \\ 1 & 0 \end{vmatrix} \quad (24)$$

containing resonance parameters of individual weak bonds  $C_1-C_4$  and  $C_2-C_3$ , as indicated by superscripts (1-4) and (2-3), respectively. Moreover, the components  $\mathbf{B}^{(1-4)}(Q_1)$  and  $\mathbf{B}^{(2-3)}(Q_1)$  resemble the relevant matrix of the linear butadiene [20]. An analogous partition of the matrix  $\mathbf{G}_{(1)}(Q_1)$  takes the form

$$\mathbf{G}_{(1)}(Q_1) = \mathbf{G}_{(1)}^{(1-4)}(Q_1) + \mathbf{G}_{(1)}^{(2-3)}(Q_1) = -\frac{\gamma}{4} \begin{vmatrix} 0 & -1 \\ 1 & 0 \end{vmatrix} - \frac{\gamma}{4} \begin{vmatrix} 0 & 1 \\ -1 & 0 \end{vmatrix}. \quad (25)$$

The second order energy  $\mathcal{E}_{(2)}(Q_1)$  is then representable as follows

$$\mathcal{E}_{(2)}(Q_1) = \mathcal{E}_{(2)}^{(1-4)}(Q_1) + \mathcal{E}_{(2)}^{(2-3)}(Q_1) + \mathcal{E}_{(2)}^{(cycl)}(Q_1), \quad (26)$$

where

$$\mathcal{E}_{(2)}^{(1-4)}(Q_1) = 4Tr(\mathbf{G}_{(1)}^{(1-4)} \cdot \mathbf{G}_{(1)}^{(1-4)+}), \quad \mathcal{E}_{(2)}^{(2-3)}(Q_1) = 4Tr(\mathbf{G}_{(1)}^{(2-3)} \cdot \mathbf{G}_{(1)}^{(2-3)+}) \quad (27)$$

are the contributions of individual C–C bonds. Meanwhile, the last term of Eq.(26) takes the form

$$\mathcal{E}_{(2)}^{(cycl)}(Q_1) = 4Tr(\mathbf{G}_{(1)}^{(1-4)} \cdot \mathbf{G}_{(1)}^{(2-3)+} + \mathbf{G}_{(1)}^{(2-3)} \cdot \mathbf{G}_{(1)}^{(1-4)+}) \quad (28)$$

and may be interpreted as the cyclization energy of the circuit  $Q_1$ . [Besides, this term may be traced back to the so-called roundabout pathways over BOs [49, 50]]. Substituting the expressions for  $\mathbf{G}_{(1)}^{(1-4)}$  and  $\mathbf{G}_{(1)}^{(2-3)}$  of Eq.(25) into Eqs.(27) and (28) shows the energy components to take the following values

$$\mathcal{E}_{(2)}^{(1-4)}(Q_1) = \mathcal{E}_{(2)}^{(2-3)}(Q_1) = \frac{\gamma^2}{2}, \quad \mathcal{E}_{(2)}^{(cycl)}(Q_1) = -\gamma^2. \quad (29)$$

so that each C–C bond contributes  $\gamma^2/2$  to the second order energy  $\mathcal{E}_{(2)}(Q_1)$  in accordance with the above-discussed rule. Again, the total increment of both C–C bonds coincides with the absolute value of the (negative) cyclization energy  $\mathcal{E}_{(2)}^{(cycl)}(Q_1)$  and, consequently, the correction  $\mathcal{E}_{(2)}(Q_1)$  vanishes. Thus, the second order destabilization of the circuit  $Q_1$  due to cyclization is now even more evident.

The four-membered circuit  $Q_2$  (Fig. 4) also may be studied similarly, where  $N = N' = 4$  and  $\mathcal{E}_{(0)}(Q_2) = 8$ . Further, pairs of neighboring C=C bonds build up linear butadiene-like fragments in the circuit  $Q_2$  in contrast to  $Q_1$ , and, consequently, the relevant BBOs and ABOs interact directly. As a result, both the first order matrix  $\mathbf{G}_{(1)}(Q_2)$  and its derivative  $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(Q_2)$  are non-zero matrices, viz.

$$\mathbf{G}_{(1)}(Q_2) = -\frac{\gamma}{4} \begin{vmatrix} 0 & 1 & 0 & -1 \\ -1 & 0 & 1 & 0 \\ 0 & -1 & 0 & 1 \\ 1 & 0 & -1 & 0 \end{vmatrix}, \quad \mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(Q_2) = \frac{\gamma^2}{16} \begin{vmatrix} 2 & 0 & -2 & 0 \\ 0 & 2 & 0 & -2 \\ -2 & 0 & 2 & 0 \\ 0 & -2 & 0 & 2 \end{vmatrix} \quad (30)$$

and yield the following energy increments

$$\mathcal{E}_{(2)}(Q_2) = 2\gamma^2, \quad \mathcal{E}_{(4)}^{(-)}(Q_2) = -\frac{32\gamma^4}{64}. \quad (31)$$

Thus, the second order energy  $\mathcal{E}_{(2)}(Q_2)$  coincides with the four-fold increment of a single C–C bond ( $\gamma^2/2$ ) in accordance with our rule.

In contrast to  $\mathbf{G}_{(1)}(Q_2)$  of Eq.(30), the second order matrix  $\mathbf{G}_{(2)}(Q_2)$  vanishes for the circuit  $Q_2$ . The underlying reason is that mediating effects of the intervening C=C bonds cancel out one another when building up elements of the matrix  $\mathbf{G}_{(2)}(Q_2)$  referring to BOs of second-neighboring C=C bonds. For example, the mediating effects of BOs of  $C_2=C_6$  and  $C_4=C_8$  bonds are of coinciding absolute values and of opposite signs in the expression for the element  $\mathbf{G}_{(2)13}(Q_2)$ . Consequently, both the third order energy  $\mathcal{E}_{(3)}(Q_2)$  and the fourth order stabilizing component  $\mathcal{E}_{(4)}^{(+)}(Q_2)$  also take zero values. The total fourth order energy  $\mathcal{E}_{(4)}(Q_2)$  then coincides with  $\mathcal{E}_{(4)}^{(-)}(Q_2)$  of Eq.(31) and is a negative quantity, i.e.

$$\mathcal{E}_{(4)}(Q_2) = -\frac{32\gamma^4}{64}. \quad (32)$$

If we recall that the acyclic isomer of octatetraene is characterized by a positive fourth order energy  $2\gamma^4/64$  [20], the above result implies a fourth order destabilization of the circuit  $Q_2$ . Partition of the correction  $\mathcal{E}_{(4)}(Q_2)$  into increments of cyclic and acyclic origin (like that performed for  $\mathcal{E}_{(2)}(Q_1)$ ) shows that the cyclization energy of the circuit  $Q_2$  equals to  $-40\gamma^4/64$ . Meanwhile, the total increment of acyclic nature coincides with  $8\gamma^4/64$ , i.e. with the four-fold contribution of a single C=C (or C–C) bond [as it was the case with the odd-membered circuits  $R_n$  [17]].

Finally, the six-membered circuit  $Q_3$  deserves some attention. Matrices both  $\mathbf{G}_{(1)}(Q_3)$  and  $\mathbf{G}_{(2)}(Q_3)$  do not vanish in this case, and this result causes no surprise. Non-zero elements, however, take distinct positions in these matrices and, consequently, the third order energy  $\mathcal{E}_{(3)}(Q_3)$  vanishes. Meanwhile, the corrections  $\mathcal{E}_{(2)}(Q_3)$  and  $\mathcal{E}_{(4)}(Q_3)$  are as follows

$$\mathcal{E}_{(2)}(Q_3) = 3\gamma^2, \quad \mathcal{E}_{(4)}(Q_3) = \frac{12\gamma^4}{64} \quad (33)$$

and coincide with respective six-fold increments of an individual C=C (or C–C) bonds. Hence, the destabilizing effect of cyclization (if any) seems to manifest itself within corrections of higher orders in this case.

Therefore, additional destabilizing contributions arise within corrections  $\mathcal{E}_{(2)}$  and  $\mathcal{E}_{(4)}$  of the circuits  $Q_1$  and  $Q_2$ , respectively, that are unambiguously related to formation of the relevant even-membered cycle. It deserves recalling here that the odd-membered circuits  $R_1$  and  $R_2$  are represented by significant stabilizing corrections  $\mathcal{E}_{(3)}(R_1)$  and  $\mathcal{E}_{(5)}(R_2)$ , respectively, that also are related to cyclization [17]. A unified viewpoint to these two conclusions allows us to formulate the following rule: A conjugated circuit (cycle) containing  $k$  C=C and  $k$  C–C bonds alternately is described by a decisive increment of the  $k$ th order ( $\mathcal{E}_{(k)}^{(cycl)}$ ) within the power series for the relevant total energy, the sign of which is determined by the parity factor  $(-1)^{k+1}$  (provided that a negative energy unit is used). The above-formulated statement evidently is nothing more than a perturbative analogue of the Hückel  $(4n + 2/4n)$  rule [1, 2]. A similar result has been obtained earlier when studying pericyclic reactions [49].

The above-obtained zero values of third order energies of the even-membered circuits  $Q_n$  ( $n=1,2,\dots$ ) support our assumption that these circuits are not among substructures responsible for distinct corrections  $\mathcal{E}_{(3)}$  of some Kekulé valence structures of biphenylene-like hydrocarbons containing the same numbers of the simplest odd-membered circuits  $R_1$  (Sect. 3). Thus, substructures playing this role are sought in the next subsection.

#### 4.2. Monocycles with exocyclic methylene groups

Let us start with 3,4-dimethylene cyclobutene denoted below by  $S_1$  (Fig. 4). Arguments for such a choice are as follows: First, Kekulé valence structures of Section 3 that were shown to be characterized by exceptionally lowered third order energies (viz. I/II, II/I, II/II, etc.), contain a circuit  $S_1$  among their substructures. Second, the circuit  $S_1$  is likely to offer a triplet of first-neighboring C=C bonds necessary for emergence of a non-zero third order energy (Sect. 2). Thus, let us consider this circuit in a more detail.

The relevant principal matrices are as follows

$$\mathbf{G}_{(1)}(S_1) = -\frac{\gamma}{4} \begin{vmatrix} 0 & 1 & 1 \\ -1 & 0 & -1 \\ -1 & 1 & 0 \end{vmatrix}, \quad \mathbf{G}_{(2)}(S_1) = -\frac{\gamma^2}{8} \begin{vmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \quad (34)$$

and deserve comparison to matrices  $\mathbf{G}_{(1)}(R_1)$  and  $\mathbf{G}_{(2)}(R_1)$  [17] representing the standard three-membered circuit  $R_1$ , viz.

$$\mathbf{G}_{(1)}(R_1) = -\frac{\gamma}{4} \begin{vmatrix} 0 & 1 & -1 \\ -1 & 0 & 1 \\ 1 & -1 & 0 \end{vmatrix}, \quad \mathbf{G}_{(2)}(R_1) = -\frac{\gamma^2}{8} \begin{vmatrix} 0 & 1 & -1 \\ -1 & 0 & 1 \\ 1 & -1 & 0 \end{vmatrix}. \quad (35)$$

It is seen that BBOs and ABOs of all pairs of C=C bonds interact directly in the structures both  $S_1$  and  $R_1$  and thereby triplets of first-neighboring C=C bonds are contained there. Moreover, matrices  $\mathbf{G}_{(1)}(S_1)$  and  $\mathbf{G}_{(1)}(R_1)$  are similar except for

signs of some elements. Finally, the same refers also to their products  $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(S_1)$  and  $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(R_1)$ . Consequences of these similarities are as follows

$$\mathcal{E}_{(2)}(S_1) = \mathcal{E}_{(2)}(R_1) = \frac{3}{2}\gamma^2, \quad \mathcal{E}_{(4)}^{(-)}(S_1) = \mathcal{E}_{(4)}^{(-)}(R_1) = -\frac{18\gamma^4}{64}. \quad (36)$$

Meanwhile, the matrix  $\mathbf{G}_{(2)}(S_1)$  differs from  $\mathbf{G}_{(2)}(R_1)$  significantly. Indeed, two non-zero elements only are present in the former matrix in contrast to the latter, namely the elements  $\mathbf{G}_{(2)12}(S_1)$  and  $\mathbf{G}_{(2)21}(S_1)$  representing the indirect interactions of orbitals of exocyclic bonds  $C_1=C_4$  and  $C_2=C_5$ . As a result, the stabilizing component of the fourth order energy  $\mathcal{E}_{(4)}^{(+)}(S_1)$  also is accordingly lower as compared to  $\mathcal{E}_{(4)}^{(+)}(R_1)$  as exhibited below in Eq.(37). Another distinctive feature of the circuit  $S_1$  consists in opposite signs of elements of matrices  $\mathbf{G}_{(2)}(S_1)$  and  $\mathbf{G}_{(1)}(S_1)$  contributing to the correction  $\mathcal{E}_{(3)}(S_1)$  and thereby in negative signs of products  $\mathbf{G}_{(2)12}(S_1) \cdot \mathbf{G}_{(1)12}(S_1)$  and  $\mathbf{G}_{(2)21}(S_1) \cdot \mathbf{G}_{(1)21}(S_1)$ . Consequently, the third order energy of the circuit  $S_1$  also is a negative quantity (see Eq.(37)). Since the decisive indirect interactions  $\mathbf{G}_{(2)12}(S_1)$  and  $\mathbf{G}_{(2)21}(S_1)$  are mediated here by BOs of the endocyclic ( $C_3=C_6$ ) bond, the negative sign of  $\mathcal{E}_{(3)}(S_1)$  may be also traced back to the destabilizing mediating effect of BOs of this particular bond. By contrast, all products of matrix elements contained in the expression for  $\mathcal{E}_{(3)}(R_1)$  are of positive signs and this consequently refers to the correction itself. Thus, the circuit  $R_1$  offers us an example of the positive mediating effect of BOs of the remaining bond (e.g. of  $C_3=C_6$ ) in the indirect interactions between those of any pair of first-neighboring  $C=C$  bonds (i.e. of  $C_1=C_4$  and  $C_2=C_5$ ) [Distinction between a positive mediating effect and a negative one proves to be especially useful if the structure under study contains a combination of both circuits  $R_1$  and  $S_1$  (Section 5)]. Let us now collect the above-discussed energy increments

$$\begin{aligned} \mathcal{E}_{(3)}(S_1) &= -\frac{1}{4}\gamma^3, & \mathcal{E}_{(4)}^{(+)}(S_1) &= \frac{8\gamma^4}{64}, & \mathcal{E}_{(4)}(S_1) &= -\frac{10\gamma^4}{64}, \\ \mathcal{E}_{(3)}(R_1) &= \frac{3}{4}\gamma^3, & \mathcal{E}_{(4)}^{(+)}(R_1) &= \frac{24\gamma^4}{64}, & \mathcal{E}_{(4)}(R_1) &= \frac{6\gamma^4}{64} \end{aligned} \quad (37)$$

and note that the corrections  $\mathcal{E}_{(3)}(S_1)$  and  $\mathcal{E}_{(3)}(R_1)$ , as well as  $\mathcal{E}_{(4)}(S_1)$  and  $\mathcal{E}_{(4)}(R_1)$  are of comparable absolute values. This allows us to expect that the circuit(s)  $S_1$  (if any) participate(s) in the formation of both third and fourth order energies of the relevant Kekulé valence structures of biphenylene-like hydrocarbons.

The four-membered circuit  $S_2$  containing four exocyclic methylenes (Fig. 4) also deserves our attention. As with the above-considered four-membered circuit  $Q_2$ , the new circuit  $S_2$  also is characterized by a zero second order matrix  $\mathbf{G}_{(2)}(S_2)$ . Interpretation of this result is similar to that referring to the former circuit  $Q_2$ . The relevant energy corrections are then as follows

$$\mathcal{E}_{(2)}(S_2) = \mathcal{E}_{(2)}(Q_2) = 2\gamma^2, \quad \mathcal{E}_{(3)}(S_2) = 0, \quad \mathcal{E}_{(4)}(S_2) = \mathcal{E}_{(4)}(Q_2) = -\frac{32\gamma^4}{64} \quad (38)$$

and coincide with those of  $Q_2$  to within fourth order terms inclusive (see Eqs.(31) and (32)). This implies that the circuit  $S_2$  (if any) is able to make a negative contribution to the fourth order energy of the given Kekulé valence structure.

The substructures  $S_1$  and  $S_2$  actually are present in certain combinations with the standard CCs  $R_n$  and  $Q_n$  ( $n = 1, 2, \dots$ ) in the individual Kekulé valence structures of Section 3. In this connection, we will consider some typical examples of "cooperation" between circuits of different series in making up separate energy corrections in the next Section.

### 5. Increments of individual conjugated circuits to stabilities of some selected Kekulé valence structures

Simplest combinations of CCs of different series arise in the Kekulé valence structures V/I, V/II and V/III of benzocyclobutene V (Fig. 5), all of them containing four C=C bonds ( $N = 4$ ) as it was the case with  $Q_2$ . Meanwhile, the relevant number of C—C bonds is now higher ( $N' = 5$ ). The usual relation between the second order energy ( $\mathcal{E}_{(2)}$ ) and the parameter  $N'$  (Sect. 2) yields  $5\gamma^2/2$ . This value is referred to below as the anticipated one.

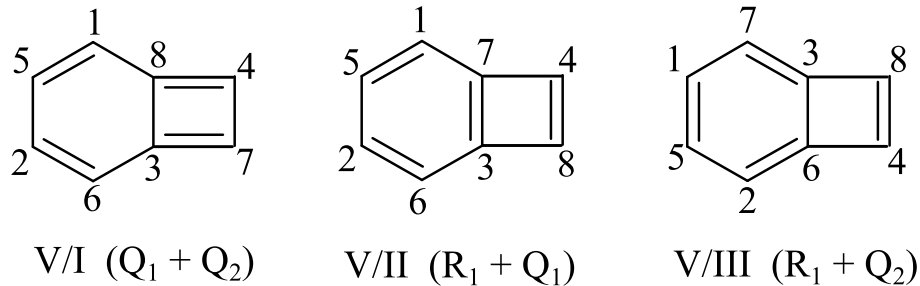


Figure 5: Kekulé valence structures of benzocyclobutene (V) along with their compositions in terms of standard conjugated circuits  $R_n$  and  $Q_n$ ,  $n = 1, 2, \dots$ . Numbers of carbon atoms and/or of their  $2p_z$  AOs also are shown.

Let us start with the structure V/I containing CCs of the  $Q_n$  series only, viz.  $Q_1$  and  $Q_2$ . This structure may be also alternatively regarded as a "perturbed" circuit  $Q_2$ , where the "perturbation" consists in the emergence of an additional bond  $C_3-C_8$  and thereby in the formation of the additional circuit  $Q_1$ . The overall set of energy increments is then as follows

$$\mathcal{E}_{(2)}(V/I) = \frac{3}{2}\gamma^2, \quad \mathcal{E}_{(3)}(V/I) = 0, \quad \mathcal{E}_{(4)}(V/I) = \mathcal{E}_{(4)}^{(-)}(V/I) = -\frac{14\gamma^4}{64}. \quad (39)$$

To comment these results, let us invoke the relevant principal matrices. The first order matrix  $\mathbf{G}_{(1)}(V/I)$  and its derivative  $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(V/I)$  take the forms

$$\mathbf{G}_{(1)}(V/I) = -\frac{\gamma}{4} \begin{vmatrix} 0 & 1 & 0 & -1 \\ -1 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{vmatrix}, \quad \mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(V/I) = \frac{\gamma^2}{16} \begin{vmatrix} 2 & 0 & -1 & 0 \\ 0 & 2 & 0 & -1 \\ -1 & 0 & 1 & 0 \\ 0 & -1 & 0 & 1 \end{vmatrix}. \quad (40)$$

It is seen that the matrix  $\mathbf{G}_{(1)}(V/I)$  contains zero elements in the positions 3,4 and 4,3 referring to the circuit  $Q_1$ . This fact is in line with the vanishing matrix



$\mathbf{G}_{(1)}(Q_1)$  (see Eq.(22)). Comparison of the matrix  $\mathbf{G}_{(1)}(V/I)$  to  $\mathbf{G}_{(1)}(Q_2)$  of Eq.(30), in turn, shows that the total number of non-zero elements becomes lower due to the above-described "perturbation". The relevant second order energy  $\mathcal{E}_{(2)}(V/I)$  also is accordingly decreased by  $\gamma^2/2$  as compared to  $\mathcal{E}_{(2)}(Q_2)$  of Eq.(31). Moreover, the difference between the actual value of  $\mathcal{E}_{(2)}(V/I)$  and the anticipated one ( $5\gamma^2/2$ ) equals to  $\gamma^2$  and thereby coincides with the relevant (negative) cyclization energy  $\mathcal{E}_{(2)}^{(c)}(Q_1)$  of Eq.(29). Hence, a second order destabilization may be concluded to take place in the structure V/I that is entirely due to the presence of the two-membered circuit  $Q_1$ .

As opposed to matrices of Eq.(40), the remaining matrix  $\mathbf{G}_{(2)}(V/I)$  vanishes as it was the case with  $\mathbf{G}_{(2)}(Q_2)$  (Subsect. 4.1). As a result, the third order energy  $\mathcal{E}_{(3)}(V/I)$  also takes a zero value. This fact is in line with vanishing corrections  $\mathcal{E}_{(3)}(Q_1)$  and  $\mathcal{E}_{(3)}(Q_2)$  (Subsect. 4.1) and causes no surprise. A zero stabilizing component ( $\mathcal{E}_{(4)}^{(+)}(V/I)$ ) of the fourth order energy is another implication of the equality  $\mathbf{G}_{(2)}(V/I) = \mathbf{0}$ . Thus, the systems V/I and  $Q_2$  are similar in respect of vanishing fourth order stabilization too. By contrast, the relevant destabilizing components differ one from another significantly as comparison of Eqs.(31) and (39) shows, viz. the absolute value of  $\mathcal{E}_{(4)}^{(-)}(V/I)$  coincides with almost a half of that of  $\mathcal{E}_{(4)}^{(-)}(Q_2)$ . This is because the zero elements  $\mathbf{G}_{(1)34}$  and  $\mathbf{G}_{(1)43}$  determine lower absolute values of those of the matrix  $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(V/I)$  as compared to  $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(Q_2)$  (see Eqs.(30) and (40)). Consequently, emergence of the additional circuit  $Q_1$  contributes to suppression of the fourth order destabilization caused by the circuit  $Q_2$  in the structure V/I.

Let us now turn to the structure V/II containing CCs of both  $4n + 2$  and  $4n$  series, namely  $R_1$  and  $Q_1$ . The relevant matrices  $\mathbf{G}_{(1)}(V/II)$  and  $\mathbf{G}_{(2)}(V/II)$  are as follows

$$\mathbf{G}_{(1)}(V/II) = -\frac{\gamma}{4} \begin{vmatrix} 0 & 1 & -1 & 0 \\ -1 & 0 & 1 & 0 \\ 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{vmatrix}, \mathbf{G}_{(2)}(V/II) = -\frac{\gamma^2}{8} \begin{vmatrix} 0 & 1 & -1 & 1 \\ -1 & 0 & 1 & -1 \\ 1 & -1 & 0 & 0 \\ -1 & 1 & 0 & 0 \end{vmatrix}. \quad (41)$$

As with the former first order matrix  $\mathbf{G}_{(1)}(V/I)$ , the new one ( $\mathbf{G}_{(1)}(V/II)$ ) also contains zero elements in the positions 3,4 and 4,3 referring to the two-membered circuit  $Q_1$ . Moreover, total numbers of non-zero elements are uniform in both matrices  $\mathbf{G}_{(1)}(V/I)$  and  $\mathbf{G}_{(1)}(V/II)$  along with the consequent second order energies (see Eqs. (39) and (42)). Finally, the energy  $\mathcal{E}_{(2)}(V/II)$  is lowered by  $\gamma^2$  as compared to the anticipated value ( $5\gamma^2/2$ ) as previously. Thus, a second order destabilization may be concluded to take place in the structure V/II too that may be traced back to the presence of the circuit  $Q_1$ . Besides, an analogous state of things refers also to  $Q_1$ -containing structures of Section 3.

Let us return again to Eq.(41) and note that the non-zero part (block) of the matrix  $\mathbf{G}_{(1)}(V/II)$  resembles that of the circuit  $R_1$  (see Eq. (35)) in accordance with the expectation. The same then accordingly refers to the non-zero block of the product  $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(V/II)$ . Implications of these similarities are as follows

$$\mathcal{E}_{(2)}(V/II) = \mathcal{E}_{(2)}(R_1) = \frac{3}{2}\gamma^2, \quad \mathcal{E}_{(4)}^{(-)}(V/II) = \mathcal{E}_{(4)}^{(-)}(R_1) = -\frac{18\gamma^4}{64}. \quad (42)$$

By contrast, the second order matrix  $\mathbf{G}_{(2)}(V/II)$  of Eq.(41) contains non-zero "intercircuit" elements in the positions 1,4[4,1] and 2,4[4,2]. These elements represent new stabilizing indirect interactions that emerge in the structure V/II. Although these extra elements exert no influence upon the third order energy [because of zero products like  $\mathbf{G}_{(2)14} \cdot \mathbf{G}_{(1)14}$ ] and the correction  $\mathcal{E}_{(3)}(V/II)$  keeps to coincide with  $\mathcal{E}_{(3)}(R_1)$  (see Eq.(43)), the stabilizing fourth order energy component  $\mathcal{E}_{(4)}^{(+)}(V/II)$  grows significantly vs.  $\mathcal{E}_{(4)}^{(+)}(R_1) = 24\gamma^4/64$  [17]. The same then accordingly refers to total values of fourth order energies. We therefore obtain

$$\mathcal{E}_{(3)}(V/II) = \mathcal{E}_{(3)}(R_1) = \frac{3}{4}\gamma^3, \quad \mathcal{E}_{(4)}^{(+)}(V/II) = \frac{40\gamma^4}{64}, \quad \mathcal{E}_{(4)}(V/II) = \frac{22\gamma^4}{64}. \quad (43)$$

Hence, the high (positive) value of the fourth order energy of the structure V/II is entirely due to an additional stabilizing increment of the intercircuit origin. The relatively high fourth order energies of the  $R_1+Q_1$ -containing Kekulé valence structures of biphenylene-like hydrocarbons (Section 3) also may be rationalized similarly.

Let us dwell now on the last structure of benzocyclobutene V/III, containing the standard circuits  $R_1$  and  $Q_2$ . The relevant principal matrices are as follows

$$\mathbf{G}_{(1)}(V/III) = -\frac{\gamma}{4} \begin{vmatrix} 0 & 1 & -1 & 0 \\ -1 & 0 & 1 & 1 \\ 1 & -1 & 0 & -1 \\ 0 & -1 & 1 & 0 \end{vmatrix}, \quad \mathbf{G}_{(2)}(V/III) = -\frac{\gamma^2}{8} \begin{vmatrix} 0 & 1 & -1 & 1 \\ -1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{vmatrix}$$

$$\mathbf{G}_{(1)}\mathbf{G}_{(1)}^{+}(V/III) = \frac{\gamma^2}{16} \begin{vmatrix} 2 & -1 & -1 & -2 \\ -1 & 3 & -2 & 1 \\ -1 & -2 & 3 & 1 \\ -2 & 1 & 1 & 2 \end{vmatrix}, \quad (44)$$

whereas the energy corrections concerned take the form

$$\begin{aligned} \mathcal{E}_{(2)}(V/III) &= \frac{5}{2}\gamma^2, \quad \mathcal{E}_{(3)}(V/III) = \frac{2}{4}\gamma^3, \quad \mathcal{E}_{(4)}^{(+)}(V/III) = \frac{16\gamma^4}{64}, \\ \mathcal{E}_{(4)}^{(-)}(V/III) &= -\frac{50\gamma^4}{64}, \quad \mathcal{E}_{(4)}(V/III) = -\frac{34\gamma^4}{64}. \end{aligned} \quad (45)$$

It is seen that the number of non-zero elements of the matrix  $\mathbf{G}_{(1)}(V/III)$  coincides with the relevant two-fold actual number of C–C bonds ( $2N_l$ ) in contrast to the former matrices  $\mathbf{G}_{(1)}(V/II)$  and  $\mathbf{G}_{(1)}(V/I)$ . The resulting second order energy  $\mathcal{E}_{(2)}(V/III)$  also accordingly equals to the anticipated value ( $5\gamma^2/2$ ). This implies that the structure V/III is the most stable one in the case of benzocyclobutene (V), the overall order of stability being  $V/III \downarrow V/II \downarrow V/I$ . Besides, the structure V/III also may be regarded as a "perturbed" circuit  $Q_2$ . In contrast to the former case of V/I, however, formation of the new bond  $C_3-C_6$  is now accompanied by emergence of an additional pair of C=C bonds, the BOs of which interact directly (viz.  $C_2=C_6$  and  $C_3=C_7$ ), and, consequently, the relevant second order energy is higher as compared to  $\mathcal{E}_{(2)}(Q_2)$ .

The second order matrix  $\mathbf{G}_{(2)}(V/III)$  of Eq.(44) exhibits even more surprising properties. Indeed, this matrix contains zero elements in the positions 2,3 and 3,2 so that no submatrix (block) like  $\mathbf{G}_{(2)}(R_1)$  arises there in spite of the presence of the circuit  $R_1$  in the structure concerned. A more detailed analysis of expressions for elements  $\mathbf{G}_{(2)23}(V/III)$  shows that mediating increments of BOs of bonds  $C_1=C_5$  and  $C_4=C_8$  are of the same absolute values and of opposite signs and thereby cancel out one another. This result causes little surprise if we recall (i) additivity of any second order element  $\mathbf{G}_{(2)il}$  with respect to mediators seen from Eq.(8) and (ii) opposite signs of mediating effects of BOs of endocyclic C=C bonds in the isolated circuits  $R_1$  and  $S_1$  (Subsect. 4.2). The above-discussed zero elements  $\mathbf{G}_{(2)23}(V/III)$ , in turn, imply vanishing products like  $\mathbf{G}_{(2)23}\mathbf{G}_{(1)23}$  in the final formula for the third order energy  $\mathcal{E}_{(3)}(V/III)$ . The actual value of the latter then coincides with  $2\gamma^3/4$  instead of  $3\gamma^3/4$  representing the circuit  $R_1$  (see Eq. (37)). Moreover, the energy concerned proves to be additive with respect to transferable increments of the circuits  $R_1$  and  $S_1$ , viz.

$$\mathcal{E}_{(3)}(V/III) = \mathcal{E}_{(3)}(R_1) + \mathcal{E}_{(3)}(S_1), \quad (46)$$

where components of the right-hand side are of opposite signs. Hence, the circuit  $S_1$  undoubtedly is among substructures determining the third order energy of the most stable Kekulé valence structure of benzocyclobutene (V/III). Finally, the above-outlined scheme of formation is easily transferable to third order energies of  $S_1$ -containing structures of both biphenylene (I/II) and related hydrocarbons (II/II, III/I, etc.).

The fourth order energy  $\mathcal{E}_{(4)}(V/III)$  of Eq.(45) also deserves some attention. As with the former structures V/I and V/II, the overall relation between this energy and the CCs contained is much less straightforward as compared to the above-discussed simple relations for  $\mathcal{E}_{(2)}(V/III)$  and  $\mathcal{E}_{(3)}(V/III)$ . Nevertheless, there are arguments for a conclusion that the non-standard circuit  $S_1$  participates in the formation of the correction  $\mathcal{E}_{(4)}(V/III)$  too: First, the actual value of this correction ( $-34\gamma^4/64$ ) is considerably closer to the sum of increments of three circuits ( $R_1$ ,  $Q_2$  and  $S_1$ ) rather than of two ones ( $R_1$  and  $Q_2$ ) [these sums correspondingly coincide with  $-36\gamma^4/64$  and  $-26\gamma^4/64$ ]. The second argument follows from comparison of fourth order energies of all Kekulé valence structures of benzocyclobutene. Indeed, the relative values of these corrections [i.e.  $\mathcal{E}_{(4)}(V/II) > \mathcal{E}_{(4)}(V/I) > \mathcal{E}_{(4)}(V/III)$ ] are consistent with the increasing total number of "destabilizing" contributors, namely with zero, one (i.e.  $Q_2$ ) and two (i.e.  $Q_2$  and  $S_1$ ), respectively.

As already mentioned, the four-membered circuit  $S_2$  (Fig. 4) also is able to contribute to fourth order energies of the relevant Kekulé valence structures. The most stable structure of biphenylene (I/I) (Section 3) offers us an example, wherein a circuit  $S_2$  is present in combination with the standard ones ( $2R_1+Q_3$ ). Comparison of the actual (i.e. of zero) value of the correction  $\mathcal{E}_{(4)}(I/I)$  (see Eq.(11)) to anticipated values following from different additive schemes support our expectation about importance of the circuit  $S_2$ : Summing up the increments of the standard circuits only [i.e. of  $2\mathcal{E}_{(4)}(R_1)$  and  $\mathcal{E}_{(4)}(Q_3)$ ] yields  $24\gamma^4/64$  (see Eqs.(33) and (37)), whilst a subsequent addition of  $\mathcal{E}_{(4)}(S_2)$  of Eq.(38) results into  $-8\gamma^4/64$ , the latter outcome being much closer to the actual zero value. To strengthen these arguments, let us consider the principal matrices of the structure I/I in a more detail.

The first order matrix  $\mathbf{G}_{(1)}(I/I)$  contains two  $3\times 3$  -dimensional blocks in its

diagonal positions that represent individual circuits  $R_1$  and coincide with the matrix  $\mathbf{G}_{(1)}(R_1)$  of Eq.(35) in accordance with the expectation. So far as the off-diagonal blocks of the same matrix are concerned, non-zero elements (either 1 or  $-1$ ) stand here in the positions 1,6[6,1] and 3,4[4,3]. These "intercircuit" elements determine an increase of the second order energy of the structure I/I as compared to  $2\mathcal{E}_{(2)}(R_1)$  (see Eqs.(9) and (36)). Further, the second order matrix of the structure I/I is as follows

$$\mathbf{G}_{(2)}(I/I) = -\frac{\gamma^2}{8} \begin{vmatrix} 0 & -1 & 1 & 0 & -1 & 0 \\ 1 & 0 & -1 & 1 & 0 & -1 \\ -1 & 1 & 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 & 1 & -1 \\ 1 & 0 & -1 & -1 & 0 & 1 \\ 0 & 1 & 0 & 1 & -1 & 0 \end{vmatrix} \quad (47)$$

and accordingly contains two submatrices like  $\mathbf{G}_{(2)}(R_1)$  of Eq.(35) in its principal diagonale. Since non-zero elements take distinct positions in the off-diagonal blocks of matrices  $\mathbf{G}_{(2)}(I/I)$  and  $\mathbf{G}_{(1)}(I/I)$ , these blocks make no contributions to the third order energy  $\mathcal{E}_{(3)}(I/I)$  and the latter coincides with the two-fold increment of an individual circuit  $R_1$  (see Eqs.(10) and (37)). More importantly, the matrix  $\mathbf{G}_{(2)}(I/I)$  contains zero elements in the positions 1,4[4,1], 1,6[6,1], 3,4[4,3] and 3,6[6,3] referring to the substructure  $S_2$  (Fig. 1) [Elements  $\mathbf{G}_{(2)13}(I/I)$  and  $\mathbf{G}_{(2)46}(I/I)$  (along with their counterparts in the positions 3,1 and 6,4, respectively) make an exception owing to additional mediating effects of the second and fifth C=C bonds]. Consequently, the total number of significant elements is relatively low in the matrix  $\mathbf{G}_{(2)}(I/I)$ . The same evidently refers to the stabilizing component of the fourth order energy  $\mathcal{E}_{(4)}^{(+)}(I/I)$  and thereby to the total correction  $\mathcal{E}_{(4)}(I/I)$  itself. Hence, participation of the circuit (substructure)  $S_2$  in the formation of the fourth order energy  $\mathcal{E}_{(4)}(I/I)$  is beyond any doubt.

## 6. Conclusions

The principal achievement of the present study consists in revealing how various aspects of constitution of individual Kekulé valence structures of biphenylene-like hydrocarbons are reflected in their total pi-electron energies and thereby in relative stabilities. Sseparate members of the power series for these energies are shown to be governed by the following rules:

1) Zero order energies are uniform for all Kekulé valence structures of the same hydrocarbon, whereas the relevant first order corrections vanish.

2) Second order energies of the  $Q_1$ -containing Kekulé valence structures are lowered by  $M\gamma^2$  as compared to those of the remaining ( $Q_1$  -free) structures, where  $M$  stands for the number of the circuits  $Q_1$ . This decrease is unambiguously traced back to the destabilizing influence of just these simplest even-membered circuits.

3) Third order energies of Kekulé valence structures of biphenylene-like hydrocarbons ( $\mathcal{E}_{(3)}$ ) are additive quantities with respect to transferable increments of the standard three-membered CCs  $R_1$  and of the newly-introduced circuits  $S_1$ , correspondingly coinciding with  $3\gamma^3/4$  and  $-\gamma^3/4$ . As a result, the circuit(s)  $S_1$  (if any) exert(s) destabilizing influence(s) upon the third order energies of the relevant Kekulé valence structures. These energies are then exceptionally reduced vs. the

anticipated values following from the relation  $\varepsilon_{(3)} = 3\gamma^3 K/4$  established previously for benzenoid hydrocarbons ( $K$  stands here for the number of the standard circuits  $R_1$ ).

4) Fourth order energies of the  $Q_2$ -containing Kekulé valence structures take relatively low (negative) values mainly because of the destabilizing influence just of the four-membered conjugated circuit(s)  $Q_2$ .

As opposed to the simple and exact form of the first three rules, the last one is of an approximate nature only. This is because presence (or absence) of the circuit  $Q_2$  is not the only factor determining the actual value of the fourth order correction and other peculiarities of the Kekulé valence structure concerned also are able to play an important role here. In this respect, two additional rules may be added here:

5) Kekulé valence structures of biphenylene-like hydrocarbons containing the simplest standard circuits  $R_1$  and  $Q_1$  possessing a single common  $C=C$  bond are characterized by an excessive fourth order stabilization of the intercircuit origin.

6) The newly-introduced circuits with two and four exocyclic  $C=C$  bonds ( $S_1$  and  $S_2$ ) also participate in the formation of the fourth order energies of the relevant Kekulé valence structures. Moreover, both circuits  $S_1$  and  $S_2$  contribute to the fourth order destabilization of the given structure along with the standard circuit(s)  $Q_2$ .

In summary, the above-formulated rules corroborate our principal hypothesis (Sect 3) about the decisive role of even-membered conjugated circuits  $Q_1$  and  $Q_2$  in the second and fourth order destabilization, respectively, of the relevant Kekulé valence structures of biphenylene-like hydrocarbons, as well as indicate the substructures (circuits)  $S_1$  and  $S_2$  (if any) to participate in the formation of the third and fourth order energies along with the standard circuits of the  $4n + 2$  and  $4n$  series ( $R_n$  and  $Q_n$ ,  $n = 1, 2, \dots$ ).

In respect of comparison of the present perturbative approach to the CC theory, the principal conclusions are as follows:

i) Total energies of individual Kekulé valence structures of biphenylene-like hydrocarbons generally differ one from another in terms of the second order of the power series (as the second rule indicates). Meanwhile, the analogous distinctions were shown to be of the third order magnitude in the case of benzenoid hydrocarbons [17] containing the circuits of the  $4n + 2$  series only. This implies that an assumption about uniform "weights" of all Kekulé valence structures is less justified for biphenylene-like hydrocarbons as compared to benzenoids. Such a conclusion, in turn, serves as a deductive accounting for less satisfactory results of the simplest version of the CC theory [based on such an assumption] in the case of non-benzenoid hydrocarbons (Section 1).

ii) The even(odd)-membered circuits  $Q_n(R_n)$ ,  $n = 1, 2, \dots$  contribute to energy corrections of even (odd) orders as the above-obtained results indicate so that participation of the former (latter) actually starts with second (third) order terms of the power series. This implies that destabilizing increments of the even-membered circuits  $Q_n$  ( $n = 1, 2, \dots$ ) generally are more important as compared to stabilizing contributions of the odd-membered ones ( $R_n$ ). Accordingly, the absolute values of parameters of CC models representing the circuits  $Q_n$  should exceed those referring to  $R_n$  for the same  $n$  value. Parameters of Ref.[14] comply with this recommendation.

iii) The approach applied allows the Kekulé valence structures of a certain bipheny

lene- like hydrocarbon to be ordered according to their total pi-electron energies and thereby relative stabilities. Thus, the present study offers an independent deductive criterion for evaluation of relative importances of individual structures. In particular, the  $S_2$ -containing structures (if any) are expected to be the most important ones [e.g. the structures I/I and IV/I of biphenylene (I) and bent [3] phenylene (IV), respectively], whereas the  $S_1$ -containing ones take the second place. [This result may be traced back to absence of "destabilizing" even-membered circuits  $Q_1$  and  $Q_2$  in the structures concerned]. Meanwhile, lowest relative stabilities and/or importances are predicted for Kekulé valence structures in which either the neighboring hexagonal rings are connected by two C=C bonds (such as I/IV) or two exocyclic C=C bonds are attached to a certain hexagonal ring (e. g. II/IV, III/V etc.). Thus, excluding of these particular structures suggested in Ref.[33] is supported by the results of the perturbative approach.

iv) The above-established participation of the newly-introduced circuits  $S_1$  and  $S_2$  (Fig. 4) in the formation of total energies and thereby relative stabilities of the relevant Kekulé valence structures of biphenylene-like hydrocarbons indicates that these substructures should be considered as supplementary conjugated circuits for these compounds and thereby should be incorporated into the relevant CC model(s).

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